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# Effective ways to enhance the photocatalytic activity of ZnO nanopowders: high crystalline degree, more oxygen vacancies, and preferential growth†

Yingying Lv, Jiayu Lin, Siyan Peng, Laijun Zhang and Leshu Yu 🕑 \*

The practical application of ZnO nanopowders (NPs) in purifying wastewater could be determined by some issues, such as low-cost and scalable preparation, high photocatalytic activity, antiphotocorrosion, and convenient recycling. In this contribution, a series of ZnO NPs were prepared in a scalable way in the 220 °C, 250 °C and 280 °C autoclaves, respectively. The structural, morphological and surface details of the samples were systematically examined by XRD, SEM, FT-IR, TEM, Raman, PL, and UV-visible spectroscopy. Along with the increase of the reaction temperature, the mean diameter of ZnO NPs increased in the range of 110-130 nm, and the color of the products was lighter, resulting in a smaller surface area but a stronger UV absorbance in the region of 200-400 nm. Moreover, the preferential growth along the (002) plane, the crystalline degree and the green emission intensity of ZnO 280 are more overt than those of ZnO 250 and ZnO 220. Some other parameters including stretching vibration and E<sub>2</sub>(high) mode of Zn-O bonding or diffraction peaks of ZnO 280 also shifted to lower wavenumbers or lower angles when compared to those of ZnO 220, revealing the existence of more oxygen vacancies in ZnO 280. As expected, ZnO 280 showed the best photocatalytic activity and antiphotocorrosion among the three samples in the degradation of rhodamine B due to the availability of abundant oxygen vacancies, preferential growth along the (002) direction and the high crystalline degree. This suggests that, along with the increase of the preparation temperature, the obtained ZnO nanopowders exhibit better photocatalytic activity. Therefore this work could provide a route to synthesize well crystalline ZnO nanopowders and open up an avenue for commercial applications of ZnO NPs in the treatment of organic wastewater.

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## 1 Introduction

Photocatalytic degradation is a typical environmental remediation method and widely used to treat organic wastewater, in which photons and a catalyst are usually involved.<sup>1</sup> Under light irradiation, the electrons from the valence band in the semiconductor are excited to the conduction band in some semiconductor materials, and electron-hole separations are created. Thereafter, the generated electron-hole pairs on the surface of the catalyst trigger the desired redox reaction between organic molecules and water or oxygen. Such a semiconductor material is commonly called the photocatalyst. To date, many photocatalytic nanomaterials have been exploited to possibly actualize the photocatalytic degradation of organic pollutants in wastewater,

such as metallic oxides (sulfides or nitrides), heterojunction nanocomposites, oxynitrides, oxysulfides, graphitic carbon nitrides, and so on.<sup>2-4</sup> In particular, intensive studies have been devoted to the synthesis, properties and prototypes of metallic oxide photocatalysts, especially for their typically representative TiO<sub>2</sub>- and ZnO-based nanomaterials due to their physical stability, nontoxicity and high catalytic activity.5

Besides having some common choices listed above, ZnO has some other evident advantages in the sense that it absorbs over a larger fraction of the UV spectrum and has a lower preparation cost in contrast to TiO<sub>2</sub>. Unfortunately, ZnO possesses the inherent drawback of the photocorrosion effect in photocatalysis, which causes fast electron-hole recombination and the decrease in photocatalytic efficiency and stability, finally limiting its practical applications.<sup>6</sup> Recently, some new techniques such as coating, hierarchical structures or doping with transition metal ions have been developed to delay photocorrosion and prevent fast electron-hole recombination.<sup>7-9</sup> But these



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School of Chemistry and Environmental Science, Key Laboratory of Polymer Preparation and Processing, Shangrao Normal University, Jiangxi, 334001, China. E-mail: vuleshu2008@126.com: Fax: +86-793-8152865: Tel: +86-793-8152865

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#### Paper

additional techniques would undoubtedly increase the cost of ZnO-based photocatalysts and ultimately hinder their practical applications in wastewater. Hence the practical application of ZnO nanopowders (NPs) in purifying wastewater needs to be considered by some issues, such as low-cost and scalable preparation, high photocatalytic activity, antiphotocorrosion, and convenient recycling.

In the past, ZnO NPs were usually prepared via wet chemical routes due to them being simple, less expensive and scalable processes, in which some Zn-containing salts were decomposed in liquid-phase reactions.<sup>10</sup> However, the obtained products suffered from either low photocatalytic activity or difficulty in recycling, probably owing to the small size, porous structure and low crystalline degree of ZnO NPs. In our previous study, ZnO NPs were cheaply prepared in a scalable way by a soluble salt-assisted route via the simple oxidation of the Zn-Na<sub>2</sub>SO<sub>4</sub> mixture. Nevertheless, the as-synthesized product was inferior to Degussa P25 in the degradation of rhodamine B (Rh-B), most probably due to the low crystalline degree of the product.<sup>11,12</sup> In our very recent work, ZnO NPs were synthesized via a simple reaction of zinc powder to H<sub>2</sub>O vapor in a 230 °C autoclave. And the as-prepared products showed good photocatalytic activity in the degradation of Rh-B under solar light irradiation, even better than that of Degussa P25.13 In this contribution, a series of ZnO NPs were prepared in a scalable way in carbondoped Teflon-lined autoclaves at 220 °C, 250 °C and 280 °C, respectively. It was found that the increasing preparation temperature led to a higher crystalline degree, more preferential growth along the (002) direction and more oxygen vacancies of the product. And these factors are greatly helpful for delaying photocorrosion and suppressing electron-hole recombination, thereby ultimately enhancing the photocatalytic activity of ZnO NPs in the process of degrading organic molecules.<sup>14–16</sup> Based on the obtained results, it is fully expected that, a higher preparation temperature up to 300 °C or even 400 °C, if the preparation conditions are permitted, might lead to the formation of better ZnO NPs in the degradation of organic wastewater. Therefore this work would provide an avenue for commercial applications of ZnO NPs in the treatment of organic wastewater.

## 2 Experimental

### 2.1 Materials preparation

The preparation procedure was similar to our recent report except for the variations of reaction temperatures in the range of 220–280 °C, and the replacement of Teflon-lined autoclaves with para polyphenol-doped Teflon-lined ones.<sup>13</sup> In detail, 5.000 g of zinc powder (steel gray, 99.99%, 200 mesh, purchased from Aladdin, seen in Fig. S1, ESI†) and a weighing bottle filled with 10 mL H<sub>2</sub>O were put into a 100 mL carbon doped Teflon-lined autoclave. The autoclave was sealed and maintained at a given temperature for 10 h in an oven and then cooled to room temperature naturally. Finally, the product was dried in an oven at 80 °C for 3 h and a colored powder (Fig. 1d) was obtained. The yield of the product was *ca.* 95–97%, based on the amount of Zn powder used. The slight loss of the product is from the transfer process.

Note: (1). Para polyphenol-doped Teflon-lined autoclaves must be used when the reaction temperature is higher than 250  $^{\circ}$ C; (2). The preparation temperature cannot be higher than 300  $^{\circ}$ C; (3). The products synthesized at 220, 250 and 280  $^{\circ}$ C correspond to ZnO 220, ZnO 250 and ZnO 280, respectively.

#### 2.2 Materials characterization

The product was systematically characterized by scanning electron microscopy (SEM; Hitachi SU8010 apparatus working at 15 kV, Japan), X-ray diffraction (XRD; Cu-Ka radiation,  $\lambda = 0.15418$  nm, Rigaku MinFlex II, Japan), Fourier transform infrared spectroscopy (FT-IR, Nicolet 6700 FT-IR spectrometer, USA, at a resolution of 2  $cm^{-1}$ ), transmission electron microscopy (TEM; JEM-2010 apparatus with an acceleration voltage of 200 kV, Japan), micro-Raman spectroscopy (LRS-5, excited with an Ar<sup>+</sup> laser at 532 nm, China), photoluminescence spectroscopy (PL, Hitachi F-7000, excited with a Xe<sup>+</sup> Lamp at 365 nm, Japan) ultraviolet-visible (UV-Vis) diffuse reflectance spectroscopy (PerkinElmer Lambda 950 spectrophotometer equipped with a diffuse reflectance accessory, USA), Brunauer-Emmett-Teller (BET) surface area analysis (Micromeritics ASAP 2460, USA), and electron balance (Metter Toledo AL104, China).

## 2.3 Photocatalytic activity of the synthesized materials

2.3.1 Degradation of Rh-B over various ZnO samples. The photocatalytic activity of ZnO samples was evaluated by the photodegradation of Rh-B aqueous solution at an initial concentration of 12 mg  $L^{-1}$  under irradiation with a 36 W mercury lamp ( $\lambda$  = 365 nm). Unless noted otherwise, 50 mg of catalyst powder was added to 35 mL of Rh-B solution in a quartz cup, corresponding to a catalyst dosage of 1.4 g  $L^{-1}$ . Before UV irradiation, the whole system was placed in the dark under magnetic stirring for 30 min to ensure adsorption/desorption equilibrium. During UV irradiation, about 2 mL aliquots were sampled at given time intervals and centrifuged. Then the top clear solution was analyzed by recording the variations of the absorption in the UV-Vis absorbance spectra of Rh-B. According to the standard curve between concentration and absorption, the value of  $(1 - C/C_0)$  was calculated, which is denoted as the degradation ratio.

**2.3.2** Photocorrosion test of various ZnO samples. 1.000 g of ZnO samples was added to a 35 mL quartz cup filled with water, and then was magnetically stirred under irradiation at 365 nm UV (36 W). After every light irradiation for 5 h, the ZnO NP turbid liquid was stood for 10 min, and dried in an oven at 100 °C after pouring away the top clear solution. The residual ZnO was weighed using an electron balance. The photocorrosion rate of ZnO samples was calculated by  $(1 - W_t)/1$ , where 1 is the initial dosage of the ZnO samples, and  $W_t$  is the residual weight of ZnO samples at every given time after photocorrosion.



Fig. 1 XRD patterns in the diffraction angle ranges of (a) 28–80° and (b) 30–38°, FT-IR spectra (c), and photography (d) of the as-prepared ZnO samples.

# 3. Results and discussion

## 3.1 Structure, surface and optical analysis of the photocatalyst

3.1.1 XRD patterns, FT-IR spectra and photographs of ZnO samples. In order to eliminate instrument error, Si powder was added into the ZnO NPs for XRD examination, and all the diffraction angles of the examined samples were calibrated by using the Si(111) crystal plane as a reference. Fig. 1a and b show the XRD patterns of the products, in which the peaks reveal the wurtzite bulk ZnO (JCPDS-36-1451) and the high crystalline degree for ZnO NPs. Moreover the  $I_{002}/I_{100}$  ratio and diffraction peak intensity of the sample increase with the preparation temperature, suggesting the more preferential growth along the (002) plane and a higher crystalline degree, since the high temperature helps in the high energy plane (002) growth of the hexagonal phase structure.<sup>17</sup> And the high activity of the (002) Zn<sup>2+</sup> face could be preferentially adsorbed by a large amount of OH<sup>-</sup> because of its positive charge. This would lead to a greater rate of production of OH• radicals, and hence enhance the photocatalytic activity of ZnO.<sup>15,18</sup> The broadening of the diffraction peaks is attributed to the small size effect of the products. And the half peak width of the samples shows a little decrease along with the increase of the reaction temperature, indicating that the size of the ZnO NPs increases with the reaction temperature. According to the Debye-Scherrer formula  $d_{(hkl)} = k\lambda/(\beta \times \cos\theta)$ , the mean diameters of the ZnO

nanoparticles along the direction of the (002) crystal plane are 112 nm, 119 nm and 130 nm, respectively. More interestingly, the diffraction peaks of ZnO 250 and ZnO 280 shift to low angles by 0.14° as compared to those of ZnO 220, showing that there is a great difference in the surface among them. The surface of the various ZnO samples was further analyzed by FT-IR spectroscopy (Fig. 1c). There is only one hump peak in the range of 300–1500 cm<sup>-1</sup>, associated with the characteristic stretching vibration mode of Zn-O bonding.<sup>19</sup> But as far as the Zn-O bonding stretching vibration is concerned, ZnO 250 and ZnO 280 show a lower wavenumber shift by 22 cm<sup>-1</sup> than ZnO 220. It goes without saying that the position of the Zn-O bonding stretching vibration is determined by the bond force constant of Zn-O bonding. It was reported that the existence of plenty of oxygen defects would weaken the Zn-O strength, thereby decreasing the bond force constant, and ultimately leading to a shift of the IR absorption peak toward low wavenumbers or of the diffraction peak toward low angles.<sup>20</sup> The absence of the absorption peak at *ca.* 3400  $\text{cm}^{-1}$  (Fig. S2, ESI<sup>†</sup>), usually attributed to the normal polymeric O-H stretching vibration of H2O, discloses that ZnO NPs absorb less water vapor and have a less mesoporous structure and a small surface area.<sup>12,14</sup> Besides, their colors also change greatly (Fig. 1d). Along with the increase of the reaction temperature, the color of the products is lighter, which is useful for permeating UV light.



Fig. 2 Raman (a) and room-temperature photoluminescence (b) spectra for the as-synthesized ZnO NPs.

The color change of the products might be closely related to the crystalline degree of the samples. The high crystalline degree, less porous structure, and small surface area of the products are also helpful for inhibiting photocorrosion.<sup>14–16</sup>

**3.1.2 Micro-Raman, PL and UV-Vis diffuse reflectance spectra of ZnO NPs.** Undoubtedly, the surface of the products could have a direct effect on their optical properties. Hence many changes in the series of the products reflected in the XRD

patterns and the FT-IR spectra could be also corroborated in the micro-Raman (Fig. 2a), PL (Fig. 2b) and UV-Vis diffuse reflectance spectra (Fig. 3).

As shown in Fig. 2a, the peaks of the ZnO nonpolar optical phonon high E2 mode and low E2 vibration are located at ca. 432–434  $\text{cm}^{-1}$  and 98  $\text{cm}^{-1}$ , respectively. And the secondorder Raman peak at 325 cm<sup>-1</sup> is also seen, arising from the Brillouin zone boundary (M point) phonon 2-E2(M). Additionally, the 198  $\text{cm}^{-1}$  peak is assigned to the double low  $E_2$  vibration. The  $E_2$  mode is usually used to analyze the stress state in films due to its high sensitivity to stress.<sup>21</sup> It is noted that the E<sub>2</sub>(high) mode of Zn-O bonding shifted to a lower wavenumber along with the increase of the preparation temperature, indicating that more defects such as oxygen vacancy  $(V_{O}^{+})$  exist in ZnO 250 or ZnO 280 than in ZnO 220.<sup>22</sup>  $V_{O}^{+}$  in ZnO not only led to the increased intra-tensile stress of the products,<sup>11</sup> but also acted as potential wells to trap electrons, and aided in electron-hole pair separation, ultimately enhancing the photocatalytic activity.<sup>15,23,24</sup> Furthermore, the luminescence properties of the products could be influenced by the oxygen vacancy in ZnO.

In Fig. 2b, the UV emission at ~383 nm corresponds to the near band edge (NBE) emission (3.2 eV, shown in Fig. 3). The green emission centered at 492 nm in the range of 450–550 nm originated from the recombination of electrons with holes trapped in singly ionized  $V_{O}^{+}$ , and is commonly seen in ZnO materials synthesized under oxygen-deficient conditions.<sup>25</sup> Moreover, the ratio of green PL intensity to NBE PL intensity increases proportionally with the preparation temperature, revealing more  $V_{O}^{+}$  content in ZnO 280 than in ZnO 280.<sup>26</sup> This is in line with the results obtained above by XRD, FT-IR and micro-Raman techniques.

Fig. 3 shows the UV-Vis diffuse reflectance spectra of ZnO NPs. It is seen that, there is higher UV absorption in ZnO 280 than in ZnO 250 or ZnO 220. So, the prepared ZnO 280 can fully use most of the UV light among the three samples, suggesting that ZnO 280 could be a more ideal photocatalyst under UV irradiation. The absorbance ranging from 400 nm to 700 nm in



Fig. 3 UV-Vis diffuse reflectance (a) spectra, and plots of  $(ah\gamma)^2$  vs. the energy of absorbed light (b) for the as-synthesized ZnO NPs.

ZnO NPs is because of the colored product (from darker color to lighter color, see photographs of ZnO NPs in Fig. 1d). The plot of  $(\alpha h\gamma)^2 vs.$  the energy of absorbed light shows that the energy of the direct allowed band gap of various ZnO NPs is 3.2 eV, which is responsible for the UV emission at ~383 nm (Fig. 2b). The absorption edges of ZnO are red-shifted (bulk ZnO, 3.36 eV at room temperature) probably due to the increased intratensile stress in the particles (also proved using the Raman spectrum in Fig. 2a).<sup>11</sup>

Overall, based on the information obtained from XRD, FT-IR, sample colors, micro-Raman, PL and UV-Vis diffuse reflectance, a conclusion was made: with the increasing preparation temperature, the synthesized ZnO NPs exhibit a better crystalline degree, more  $V_O^+$  and preferential growth along the (002) plane, which are well known to be helpful for antiphotocorrosion and the enhancement of photocatalytic activity.<sup>14–16,18,23,24,26</sup> In this contribution, ZnO 280 is the best photocatalyst.

#### 3.2 Morphological and structural observations

**3.2.1 SEM images of ZnO NPs.** Fig. 4 shows the SEM images of the products without sputtering Au or Pt films onto the surface of ZnO NPs. It is seen that many nanoparticles with a mean size of several hundred nanometers in diameter were aggregated to form a large particulate. Also, the sizes of the ZnO NP particulates correspond to the used Zn powder, indicating that most of the original Zn particulates did not break up thoroughly into many individuals after undergoing the strong reaction with water in the autoclave (Fig. S1, ESI<sup>†</sup>).



Fig. 4 SEM images of ZnO 220 (a and b), ZnO 250 (c and d) and ZnO 280 (e and f).

Furthermore, the size of the individual particulate is increasing along with the preparation temperature, and the hexagonalcross section pencil-like morphology of the products is easy to observe, in good accordance with the diffraction peak broadening and the preferential growth along the (002) plane in the XRD patterns.<sup>17</sup> The surface of the ZnO nanoparticles is very smooth and has less mesopores, which is beneficial for the antiphotocorrosion and quick sediment of ZnO, and thereby for the photocatalytic activity and recycling of the photocatalyst.<sup>13-16</sup>

**3.2.2 TEM images and SAED patterns.** The accurate size of the ZnO NPs was further confirmed by TEM (Fig. 5). It is seen that, the size of the ZnO nanoparticles (Fig. 5a, c and e) is in the range of several tens to hundreds of nanometers, and increases with the reaction temperature, which is consistent with the XRD (Fig. 1a and b) and SEM analysis (Fig. 4). The ripple-like contrast observed in the TEM images is due to the tensile-stress in ZnO NPs (also proved by the micro-Raman spectra in Fig. 2a and UV-Vis diffuse reflectance spectra in Fig. 3).<sup>27</sup> Fig. 5b, d and f show the corresponding selected area electron diffraction (SAED) patterns, and the diffraction spots are brighter and brighter along with the increase of the preparation temperature, further indicating the higher crystalline degree for ZnO 280 than ZnO 250 or ZnO 220, also in agreement with the results of



Fig. 5 TEM images of ZnO 220 (a and b), ZnO 250 (c and d) and ZnO 280 (e and f).

the XRD patterns (Fig. 1a). The bright diffraction spots in the SAED patterns are irregular because of the location of the electron beam at the grain boundaries among several ZnO nanoparticles,<sup>28</sup> and indicate the single crystal structure of ZnO nanoparticles. Besides, there are no mesopores in each ZnO nanoparticle, agreeing with the results of the FT-IR spectra (Fig. 1c) and SEM images (Fig. 4).



Fig. 6 Nitrogen adsorption–desorption isotherm of the as-prepared ZnO NPs; the insets show the corresponding BJH pore-size distribution plots.

## 3.3 BET surface area of the photocatalyst

The surface area and pore structure of the photocatalyst are directly related to its photocatalytic activity. Fig. 6 shows the corresponding nitrogen adsorption/desorption isotherms and Barrett-Joyner-Halenda (BJH) pore-size distribution curve of the ZnO NPs. These isotherms belong to Type IV H3 loops, revealing that the ZnO NPs are comprised of aggregates forming slit-like mesopores.<sup>29</sup> With the increase of the reaction temperature, the corresponding loop and BET surface area of the sample decrease, and the number of slit-like mesopores of the sample increases, both revealing that the ability of absorbing N2 becomes weaker and weaker for the sample prepared at high temperature. Moreover, the adsorption and desorption isotherms overlap more with increasing reaction temperature, which shows that the multimolecular and monomolecular adsorptions are more reversible. This is due to the larger size of the sample when increasing the reaction temperature, though having been disclosed by XRD, SEM and TEM. On the other hand, the surface area of the product can be theoretically expressed using the formula  $S_{\text{BET}} = 6000/d\rho$  (where  $\rho$  is the density of ZnO with a value of 5.8, and *d* is its average diameter of ca. 110-130 nm calculated using the Debye-Scherrer formula and also shown in Fig. 5), since there is no



**Fig. 7** Degradation ratio (a) of Rh-B over ZnO NPs under UV irradiation for different times and the corresponding kinetic study (b).

porous hole in the approximately ball-shaped ZnO nanoparticles (reflected by Fig. 1c and 5). The calculated surface area of the prepared product might be in the range of 7.95–9.23 m<sup>2</sup> g<sup>-1</sup>. Therefore, the actual surface area (6.04–6.98 m<sup>2</sup> g<sup>-1</sup>) of the products might suggest a little agglomeration of the ZnO NP powder (seen in Fig. 5a, c and e), but the agglomeration degree is less with the higher preparation temperature. This indicates that ZnO 280 is a better dispersing agent than others in a liquid reaction system and contributes to the photocatalytic reaction.

#### 3.4 Photocatalytic activity of various ZnO NPs

**3.4.1** Photocatalytic degradation of RhB over various ZnO NPs under UV irradiation. According to the characterization above, ZnO 280 has some striking traits, such as plenty of oxygen vacancies, preferential growth along the (002) direction, and a high crystalline degree. These good characteristics make ZnO 280 more promising in the treatment of organic wastewater than ZnO 250 and ZnO 220. As expected, ZnO 280, though having the smallest surface area among the three samples, showed excellent photocatalytic activity on the degradation of Rh-B, and the obtained result is shown in Fig. 7. It is seen that, the photocatalytic activity was enhanced with the preparation



Fig. 8 Photocorrosion test of ZnO NPs

temperature (Fig. 7a), and its order corresponds to the changing values of the XRD diffraction peak intensity, FT-IR wavenumber shift, PL spectra green light intensity, and UV absorbance. The Rh-B degradation was attributed to the help of ZnO samples since itself degradation was almost negligible under UV irradiation.<sup>11,13</sup> Additionally, the absorbance wavelength of the degraded solution (Fig. S3, ESI†) did not shift during 40 min of the photocatalytic process, probably indicating that the molecule of Rh-B was decomposed directly into some small molecules such as CO<sub>2</sub> and H<sub>2</sub>O, not leading to the formation of the intermediates.

The reaction kinetics was further depicted by the curve of  $\ln(C_0/C)$  vs. reaction time t, and the pseudo-first-order reaction could be inferred (Fig. 7b). The reaction rate constant (denoted as k) over ZnO 280 (0.117) is higher than that over ZnO 250 or ZnO 220 (0.096 and 0.076), also much higher than that of P25 (0.079).<sup>13</sup> Furthermore, the catalytic activity of ZnO 280 increases with the catalyst loading (Fig. S4, ESI<sup>†</sup>). The optimal catalyst dosage of ZnO 280 is as high as 14 g  $L^{-1}$ , much larger than that of P25, since the prepared ZnO in this work has a small surface area and a high density.<sup>12</sup> The photocatalytic degradation efficiency was decreased when the catalyst dosage is over 14 g  $L^{-1}$ . This could be attributed to the shadowing effect, since the high turbidity from the high concentration of ZnO 280 scatters UV light, leading to the decrease of the penetration depth of the UV light.<sup>12,30</sup> Beyond these good traits of ZnO 280, it still has other distinguishing features such as low-cost and scalable preparation (Zn powder is used), and convenient recycling (due to quick sedimentation). Therefore, ZnO 280 would also have a wide application prospect in purifying wastewater like P25.

**3.4.2** Photocorrosion test of ZnO NPs and their corresponding photocatalytic activity. Fig. 8 shows the photocorrosion test of ZnO NPs, indicating that ZnO 280 has the lowest photocorrosion rate among the three samples. After long-time UV irradiation for 20 h (equal to 30 times ZnO recycles, provided one recycle take 40 min), the diffraction peak intensity of Zn 220 decreased more than the other two samples (not shown), suggesting the high crystalline degree of the products helps to enhance antiphotocorrosion. Therefore, it is possible



Fig. 9 Degradation ratio (a) of Rh-B over photocorrosion-suffered ZnO NPs under UV irradiation for different times and the corresponding kinetic study (b).

to synthesize well crystallized ZnO by overcoming its inherent drawback of the photocorrosion effect.

Fig. 9 shows the degradation ratio of Rh-B over photocorrosionsuffered ZnO NPs under UV irradiation for different times, and the corresponding kinetic study. After suffering from 20 h of photocorrosion, nearly equal to 30 times ZnO recycles (40 min for one recycle, seen in Fig. 7a), ZnO 280 showed a little decreased degradation efficiency of Rh-B when compared with the one first used, while ZnO 250 and ZnO 220 showed a notable decreased degradation efficiency of Rh-B (Fig. 7). This is consistent with the decreased order of the XRD diffraction peak intensity (Fig. S5, ESI†). In a word, ZnO 280 has more repeated photocatalytic activity than ZnO 250 or ZnO 220 probably due to the better antiphotocorrosion.

## 4 Conclusions

A series of ZnO NPs were prepared in a scalable way in the 220  $^{\circ}$ C, 250  $^{\circ}$ C and 280  $^{\circ}$ C autoclaves, respectively. Along with the increase of the preparation temperature, the ZnO NPs showed better photocatalytic activity and antiphotocorrosion in the degradation of rhodamine B under UV irradiation, due to the existence of plenty of oxygen vacancies, preferential growth of the (002) plane, and the high crystalline degree. On account of the obtained results, it is fully speculated that, a higher synthesis temperature up to 300  $^{\circ}$ C or even 400  $^{\circ}$ C, if permitted, might lead to the formation of better ZnO NPs for the degradation of organic substances. Therefore this work would pave the way to commercial applications of ZnO NPs in the treatment of organic wastewater.

# Conflicts of interest

There are no conflicts to declare.

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